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**APPLICATION
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(Substitute Specification)**

TITLE: UNIT FOR SEPARATING GAS

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DESCRIPTION

UNIT FOR SEPARATING GAS

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TECHNICAL FIELD

[0001]

The present invention relates to a unit for separating gas, which separates each of a plurality of specific gases from a treatment gas containing the specific gases.

10

BACKGROUND ART

[0002]

Conventionally, a variety of different gases are used in semiconductor production processes, depending on the nature of the individual process. For example, PFC (perfluoro compound) gas, which includes a variety of fluorine-containing compounds such as CF₄, NF₃, C₃F₈, SF₆ and CHF₃, is used as a reactive gas in dry etching processes and thin film formation processes, and an exhaust gas containing this PFC gases is produced.

[0003]

Exhaust gases such as PFC gas cannot be simply discharged from the system, and must be treated using a variety of treatment methods. Examples of these treatment methods include (i) decomposition treatments in which the PFC gas is decomposed by combustion, catalytic heating, or plasma decomposition or the like, (ii) membrane separation in which the materials are separated by a membrane, (iii) cryogenic separation in which separation is achieved by utilizing differences in the boiling points of the gases, and (iv) adsorption treatments.

[0004]

However, there are drawbacks associated with decomposition treatments (i) in that achieving complete decomposition is difficult, and the fact that because the gas is decomposed and discharged, it cannot be recovered and reused. Furthermore, although membrane separation (ii) enables the removal of nitrogen from an exhaust gas, the separation of gases of similar molecular size such as CF₄ and NF₃ is problematic. Moreover, the aforementioned method (iii) requires an extremely large apparatus, and is very expensive in terms of both running costs and the cost of the facilities. Furthermore, the difference in boiling point between NF₃ and CF₄ is only 1°C, meaning separation of these two gases is very difficult. The method (iv) requires regular replacement of the adsorbent, which leads to costs associated with the disposal of the used adsorbent.

[0005]

Accordingly, Japanese Patent Laid-Open Publication No. 2002-273144 proposes a device for separating PFC gases that uses a chromatographic separation device packed with an activated carbon filler. The device disclosed in Japanese Patent Laid-Open Publication No. 2002-27314 is able to effectively separate CF₄ and NF₃.

[0006]

However, it was found that the device disclosed in Japanese Patent Laid-Open Publication No. 2002-27314 was unable to satisfactorily separate a mixed gas of CF₄ and C₂F₆, for example. As described above, PFC gas contains a variety of different gases, and a unit that is capable of effectively treating and separating this type of multi-component PFC gas has been keenly sought.

DISCLOSURE OF INVENTION

[0007]

The present invention provides a unit for separating
5 gas that is capable of effectively separating each of the
components from a PFC gas containing a plurality of
components.

[0008]

The present invention provides a unit for separating
10 gas, which separates each of a plurality of specific gases
from a treatment gas containing the specific gases, wherein
the unit contains a plurality of columns packed with
different fillers, and by connecting these columns in series,
and passing the treatment gas sequentially through the
15 fillers of the plurality of columns, each of the specific
gases is separated chromatographically from the treatment
gas.

[0009]

Furthermore, the present invention also provides a unit
20 for separating gas, which separates each of a plurality of
specific gases from a treatment gas containing the specific
gases, wherein the unit contains a column packed with a
plurality of different fillers, and by passing the treatment
gas through the plurality of fillers inside the column, each
25 of the specific gases is separated chromatographically from
the treatment gas.

[0010]

By conducting chromatographic separation using a
plurality of fillers in this manner, the plurality of
30 specific gases can be separated effectively.

[0011]

Furthermore, the aforementioned specific gases are preferably PFC gases discharged from semiconductor production processes, and the aforementioned treatment gas is preferably a gas that also contains nitrogen gas.

5 [0012]

Furthermore, the specific gases preferably include NF₃, CF₄, and C₂F₆, and the aforementioned fillers preferably include zeolite and activated carbon.

[0013]

10 Furthermore, the zeolite is preferably the molecular sieve 13X or an equivalent product.

[0014]

15 As described above, the present invention enables a plurality of specific gases to be separated effectively, by conducting chromatographic separation using a plurality of fillers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

20 Fig. 1 is a diagram showing the structure of an embodiment of the present invention.

Fig. 2 is a diagram showing the structure of a chromatographic separation device that uses a plurality of columns.

25 Fig. 3 is a graph showing the state of gas flow at the outlet of the first column.

Fig. 4 is a graph showing the state of gas flow at the outlet of the second column.

30 Fig. 5 is a diagram showing the structure of a chromatographic separation device that uses a single column containing a plurality of fillers.

Fig. 6 is a graph showing the state of gas flow at the outlet of the column shown in Fig. 5.

Fig. 7 is a diagram showing the structure of a test unit.

5 Fig. 8 is a diagram showing the structure of another test unit.

BEST MODE FOR CARRYING OUT THE INVENTION

[0016]

10 As follows is a description of a preferred embodiment of the present invention, based on the drawings.

[0017]

A PFC gas is supplied to a production process 10 such as an etching or thin film formation process conducted at a 15 semiconductor production plant. As a result, an exhaust gas containing the PFC gas is produced. An inlet for a suction pump 12 is connected to the path of the exhaust gas, and the exhaust gas containing the PFC gas is extracted from the production process 10 by this suction pump 12. Gases such 20 as CF₄, NF₃, C₂F₆, and SF₆ can be used as the PFC gas, and in this embodiment, the PFC gas contains CF₄, C₂F₆, and NF₃. Because the PFC gas decomposes and generates hydrofluoric acid during the production process 10, the exhaust gas also contains hydrofluoric acid. As a result, if the exhaust gas 25 is introduced directly into the suction pump 12, then there is a danger that the suction pump 12 may be damaged. Furthermore, the exhaust gas also contains metals generated during etching and the like, meaning if the exhaust gas is introduced directly into the suction pump 12, there is a 30 danger that deposits may accumulate inside the suction pump 12. Accordingly, nitrogen (N₂) gas is supplied as a diluent

gas at a point prior to the exhaust gas reaching the suction pump 12, thereby diluting the exhaust gas.

[0018]

The outlet of the suction pump 12 is connected to a
5 scrubber 14, and the nitrogen-diluted exhaust gas is supplied to the scrubber 14. This scrubber 14 uses a water shower to dissolve and remove hydrofluoric acid (HF) and any other water-soluble acidic materials contained within the exhaust gas.

10 [0019]

The exhaust gas from the scrubber 14 is then supplied to a dewatering device 16, where moisture is removed from the gas. The exhaust gas from the scrubber contains a large quantity of moisture, and it is preferable to remove this 15 moisture prior to the subsequent steps. Although any form of dewatering device can be employed as the dewatering device 16, devices that remove the moisture by lowering the temperature of the exhaust gas are preferred.

[0020]

20 The exhaust gas containing the PFC gas and nitrogen is then supplied to a concentration device 18. This concentration device 18 is used for removing the nitrogen, and is preferably a membrane separation device that employs a gas permeable membrane. This device separates the 25 nitrogen from the exhaust gas, thereby concentrating the PFC gas (the CF₄, NF₃, and C₂F₆ in this embodiment).

[0021]

Having been concentrated in this manner, the PFC gas is supplied to a chromatographic separation device 20. The 30 chromatographic separation device 20 includes a column packed with a desired filler, and the gas is passed through

this column. Because each of the gas components exhibits a different affinity (adsorption and desorption coefficient) for the filler, the retention times for each component vary, thus enabling the gas to be separated into its components.

- 5 In other words, the CF₄, NF₃, and C₂F₆ are separated. Because nitrogen gas is used as a carrier gas in the chromatographic separation, each gas is generated as a mixed gas with nitrogen.

[0022]

- 10 At this point, the mixed gas of CF₄ + nitrogen is supplied to a concentration device 22, C₂F₆ + nitrogen is supplied to a concentration device 24, and NF₃ + nitrogen is supplied to a concentration device 26. These concentration devices 22, 24 and 26 are similar to the concentration device 18 described above, and can employ membrane separation devices. Within these membrane separation devices, by employing a structure wherein the concentrated gas is either circulated a number of times, or treated in a plurality of stages, almost 100% of the nitrogen can be separated, meaning pure CF₄ gas, NF₃ gas, and C₂F₆ gas can be obtained at concentrations of 100%.
- 15
- 20

[0023]

The CF₄ gas, C₂F₆ gas, and NF₃ gas can be recovered and reused within the production process 10.

- 25 [0024]
- As described below, the chromatographic separation device 20 usually also yields a fraction that contains both CF₄ and NF₃, but the CF₄ and NF₃ can be separated by subjecting this mixed fraction to further separation, and consequently this CF₄ + NF₃ fraction has been omitted from the diagram.
- 30

[0025]

In this manner, by using the chromatographic separation device 20, the present embodiment enables CF₄, C₂F₆, and NF₃ gases to be separated effectively. Moreover, the separated 5 CF₄, C₂F₆, and NF₃ gases can be recovered and reused.

[0026]

Fig. 2 shows an example of the structure of the chromatographic separation device 20. In this example, the chromatographic separation device 20 includes two columns, 10 namely a first column 50-1 and a second column 50-2, connected together in series. The first column 50-1 is packed with a zeolite (molecular sieve 13X) 30 with a predetermined pore size, and the second column 50-2 is packed with palm shell activated carbon 32. The first 15 column 50-1 is supplied continuously with nitrogen gas (N₂), and is also supplied intermittently with the treatment gas containing CF₄, NF₃ and C₂F₆ via a valve 34. The outlet of the first column 50-1 is connected to the inlet of the second column 50-2 via a valve 36, and is also able to 20 discharge C₂F₆ gas via a valve 38. In addition, the outlet of the second column 50-2 is able to discharge CF₄ + N₂ gas via a valve 40, CF₄ + NF₃ + N₂ gas via a valve 42, NF₃ + N₂ gas via a valve 44, and nitrogen (N₂) gas via a valve 46.

[0027]

25 In this type of chromatographic separation device 20, first the valves 34, 38, 40, 42 and 44 are closed, the valves 36 and 46 are opened, and the first and second columns 50-1 and 50-2 are flushed with N₂ carrier gas. From this state, the valve 34 is opened, and a predetermined 30 quantity of the treatment gas is supplied in a pulse-like manner. This treatment gas should preferably be supplied to

the first column 50-1 with minimal dilution by the N₂ gas. Appropriate switching of the valves may also be used to temporarily halt the supply of N₂ while the treatment gas is supplied.

5 [0028]

Following the supply of the predetermined quantity of the treatment gas, the valve 34 is closed, and the supply of the N₂ gas can be recommenced. The CF₄, NF₃ and C₂F₆ within the treatment gas is separated by the molecular sieve 13X inside the first column 50-1. In other words, the C₂F₆ is slower to desorb from the molecular sieve 13X than the CF₄ and NF₃. Consequently, as shown in Fig. 3, the CF₄ + NF₃ fraction from the treatment gas appears first at the outlet of the first column 50-1, with the C₂F₆ fraction appearing considerably later.

[0029]

Accordingly, when the C₂F₆ is discharged, the valve 36 is closed and the valve 38 is opened, thus enabling separation and extraction of the C₂F₆ gas. Once extraction of the C₂F₆ has finished, the valve 38 is closed and the valve 36 is opened.

[0030]

As a result, the second column 50-2 is supplied with a treatment gas that contains CF₄ and NF₃, but contains no C₂F₆. In the second column 50-2, the CF₄ and NF₃ are separated by the activated carbon 32. In other words, the NF₃ is slower to desorb from the activated carbon than the CF₄. Consequently, as shown in Fig. 4, the CF₄ fraction from the treatment gas appears first at the outlet of the second column 50-2, with the NF₃ fraction appearing later. The CF₄ and NF₃ are not completely separated at this point, and a

mixed gas containing both components is discharged in the middle. Accordingly, when the CF₄ is discharged, the valve 46 is closed, the valve 40 is opened, and CF₄ + N₂ is collected, when CF₄ + NF₃ is discharged, the valve 40 is closed, the valve 42 is opened, and CF₄ + NF₃ + N₂ is collected, and when NF₃ is discharged, the valve 42 is closed, the valve 44 is opened, and NF₃ + N₂ is collected.

5 closed, the valve 42 is opened, and CF₄ + NF₃ + N₂ is collected, and when NF₃ is discharged, the valve 42 is closed, the valve 44 is opened, and NF₃ + N₂ is collected.

The CF₄ + NF₃ fraction may be further separated using a separate column packed with activated carbon. Alternatively,

10 the CF₄ + NF₃ + N₂ may also be returned to the treatment gas side of the separation device.

[0031]

In this manner, C₂F₆ + N₂, CF₄ + N₂, and NF₃ + N₂ fractions can be collected separately.

15 [0032]

Fig. 5 shows an alternative structure for the chromatographic separation device 20. In this example, a single column 50 is packed sequentially with zeolite (molecular sieve 13X) 30 and activated carbon 32, with the zeolite closer to the column inlet. Accordingly, the treatment gas first makes contact with the zeolite 30, and subsequently contacts the activated carbon 32.

20

[0033]

With this type of column 50, gas separation can be conducted in an almost identical manner to that described above for the series-connected first and second columns 50-1 and 50-2. This example differs from that above in that C₂F₆ also passes through the activated carbon 32, but even after passage through the activated carbon 32, C₂F₆ is still discharged after CF₄ and NF₃, meaning there is no deleterious impact on the separation performance. In other words, as

25

30

shown in Fig. 6, the fractions $\text{CF}_4 + \text{N}_2$, $\text{CF}_4 + \text{NF}_3 + \text{N}_2$, $\text{NF}_3 + \text{N}_2$, and $\text{C}_2\text{F}_6 + \text{N}_2$ appear sequentially at the outlet of the column 50. Accordingly, by opening the valves 38, 40, 42 and 44 in sequence, each of the fractions can be separated
5 and recovered. The $\text{CF}_4 + \text{NF}_3 + \text{N}_2$ fraction may be further separated using a separate column packed with activated carbon, or may be returned to the treatment gas side of the separation device. Other facets of the structure and the operation of this example are the same as those described in
10 relation to Fig. 2.

[0034]

In this manner, by using a chromatographic separation device 20 in which the treatment gas is passed sequentially through the two fillers shown in Fig. 2 and Fig. 5, CF_4 , NF_3
15 and C_2F_6 can be separated.

[0035]

In the examples shown in Fig. 2 and Fig. 5, the chromatographic separation was conducted with the zeolite 30 positioned in the former stage and the activated carbon 32 in the latter stage, but this sequence may also be reversed.
20 Furthermore, in the example of Fig. 5, the zeolite and the activated carbon may also be mixed. However, tests suggest that separating off C_2F_6 first using the zeolite 30, and then using the activated carbon 32 to separate CF_4 and NF_3 leads
25 to a reliable separation, whereas if the sequence is reversed, complete separation of NF_3 and C_2F_6 may not be possible.

[0036]

As follows is a description of the separation of CF_4
30 and C_2F_6 by the zeolite 30. In this example, a zeolite 30 with a pore size of at least 0.5 nm is used as the filler.

By using a zeolite with this type of large pore size, CF₄ and C₂F₆ can be effectively separated.

[0037]

In other words, a variety of different zeolites were
5 tested as fillers, and it was found that whereas a molecular
sieve 5A (manufactured by GL Sciences Inc.) with a pore size
of approximately 5 nm is unable to produce a satisfactory
separation, molecular sieve 13X (manufactured by GL Sciences
Inc.), and zeolite F-9 (manufactured by Tosoh Corporation),
10 which has a pore size of approximately 0.8 nm (meaning it is
unable to adsorb molecules with effective diameters greater
than 0.8 nm) and is marketed as an equivalent product to
molecular sieve 13X, are ideal for achieving separation.

[0038]

15 Currently, there are no zeolites commercially available
with a larger pore size than molecular sieve 13X, but it is
believed that a zeolite with a larger pore size than
molecular sieve 13X would also be usable, although this has
not been confirmed.

20 [0039]

For CF₄ and C₂F₆, the maximum molecular diameter,
calculated on the basis of the F-F internuclear distance and
the F electron cloud radius of 0.133 nm, is 0.4445 nm for
CF₄ and 5.69 nm for C₂F₆. For example, the maximum molecular
25 diameter for CF₄ is determined using the equation 0.1785
(the F-F internuclear distance) + 0.133 × 2 (two F).

[0040]

When molecular sieve 5A is used, it is thought that the
reason that separation of CF₄ and C₂F₆ cannot be achieved
30 reflects the fact that the pore size is smaller than the
molecular diameter of the C₂F₆. Accordingly, the pore size

of the zeolite must be larger than the maximum molecular diameter of C₂F₆.

[0041]

When this type of zeolite is used, the adsorption of CF₄ weakens, whereas the C₂F₆ continues to be adsorbed. It is thought that this effect is responsible for the reliable separation of the CF₄ and C₂F₆.

[0042]

A molecular sieve is normally used for separating molecules that are larger than the sieve pore size from molecules that are smaller, and the conducting of a separation process using a molecular sieve with a pore size that is larger than both of the separation target materials is unusual.

[0043]

In this embodiment, separation of the target materials CF₄ and C₂F₆ is achieved using a zeolite with an adsorption pore size that is larger than the maximum diameter of both CF₄ and C₂F₆.

[0044]

In this chromatographic separation device 20, nitrogen is used as a carrier gas, and by using this carrier gas to sequentially desorb and discharge the CF₄ and C₂F₆ adsorbed to the filler, the CF₄ and C₂F₆ are separated.

[0045]

In another preferred configuration, a plurality of the above chromatographic separation devices 20 are prepared, and the exhaust gas is passed sequentially through each of these chromatographic separation devices 20, with each fraction collected sequentially from each of the chromatographic separation devices 20.

[0046]

The collection of each of the component gases at the outlet of the chromatographic separation device 20, and the switching of the valves, are preferably conducted in accordance with the results of analyses performed on the gas at the outlet. For example, the different components can be detected using a quadrupole mass spectrometer (QMS), a differential thermal detector (TCD), or a Fourier transform infrared analyzer (FT-IR), with control then conducted in accordance with the results of the analysis.

EXAMPLES

[0047]

A test was conducted using a test unit with the structure shown in Fig. 7. The unit in Fig. 7 corresponds with the configuration shown in Fig. 2.

[0048]

The first column 50-1 for the test employed a column in which a 5 m long SUS pipe of outer diameter 1/8 inch was packed with a zeolite 30 comprising molecular sieve 13X (manufactured by GL Sciences Inc.) with a particle size of 60 to 80 mesh. The second column 50-2 for the test employed a column in which a 5 m long SUS pipe of outer diameter 1/8 inch was packed with an activated carbon 32 comprising palm shell activated carbon with a specific surface area of 1158 m²/g and a particle size of 60 to 80 mesh. The first and second columns 50-1 and 50-2 were connected together in series.

[0049]

Nitrogen (N₂) gas was passed through the first and second columns 50-1 and 50-2 at a flow rate of 35 mL/minute,

and a six-way cock 60 was used to introduce a mixed gas of CF₄/C₂F₆/NF₃ (CF₄:C₂F₆:NF₃ = 1:1:1) in a pulse-like manner. Furthermore, the outlets of both the first column 50-1 and the second column 50-2 were analyzed using a mass spectrometer 62. In the drawing, MFC represents a flow rate controller.

[0050]

The analysis results from the outlet of the first column 50-1 are shown in Fig. 3, and the analysis results from the outlet of the second column 50-2 are shown in Fig. 4.

[0051]

The test was conducted at 40°C, but other temperatures are also acceptable. However, because the separation properties vary depending on the temperature, the test is preferably conducted at a constant temperature.

[0052]

The test results confirmed that by using a pulsed introduction of gas, the respective peaks for the CF₄ + NF₃ mixture and C₂F₆ had completely separated by reaching the outlet of the first column 50-1, meaning that by simply selecting the sampling period, a CF₄ + NF₃ mixed gas and pure C₂F₆ could be obtained. Accordingly, the C₂F₆ was extracted, and the CF₄ + NF₃ mixed gas was fed into the second column 50-2. As a result, it was found that at the outlet of the second column 50-2, the CF₄ and NF₃ had separated by the time of discharge.

[0053]

At the outlet of the second column 50-2, pure CF₄, an unseparated CF₄ + NF₃ gas fraction, and pure NF₃ were obtained, and the unseparated gas fraction is preferably

either returned to the inlet of the series-connected first and second columns, or passed through a separate activated carbon column provided in series, to effect separation and recovery.

5 [0054]

Hence, the unit described above was confirmed as being capable of favorable recovery of CF₄, C₂F₆, and NF₃.

[0055]

(Example 2)

10 A test was conducted using a test unit with the structure shown in Fig. 8. The column 50 for the test employed a column in which a 10 m long SUS pipe of outer diameter 1/8 inch was packed first with palm shell activated carbon with a specific surface area of 1158 m²/g and a particle size of 60 to 80 mesh, and then with molecular sieve 13X (manufactured by GL Sciences Inc.) with a particle size of 60 to 80 mesh. This yielded a column such as that shown in Fig. 5, in which the zeolite (molecular sieve 13X) 30 and the activated carbon (palm shell activated carbon) 32 were arranged in sequence along the flow direction of the treatment gas. The packing ratio of the two fillers was 1:1.

20 [0056]

Nitrogen gas was passed through the column 50 at a flow rate of 35 mL/minute, and a six-way cock 60 was used to introduce a mixed gas of CF₄/C₂F₆/NF₃ (CF₄:C₂F₆:NF₃ = 1:1:1) in a pulse-like manner. The outlet of the column 50 was analyzed using a mass spectrometer 62. In the drawing, MFC represents a flow rate controller.

[0057]

30 The analysis results from the outlet are shown in Fig. 6. The test was conducted at 40°C, but other temperatures

are also acceptable. However, because the separation properties vary depending on the temperature, the test is preferably conducted at a constant temperature.

[0058]

5 The test results revealed that the peaks for CF₄, NF₃, and C₂F₆ appeared sequentially at the outlet of the column 50, confirming that each of the gases could be separated. The unseparated CF₄ + NF₃ fraction can be separated by passage through a subsequent, separate activated carbon column.

10 [0059]

The width of the peaks and the level of overlap of the unseparated portion vary depending on the concentration of the supplied gas, but a satisfactory separation can be achieved by altering the packing ratio (in this example 1:1) 15 of the fillers packed inside the single column.

[0060]

In this manner, the unit described above was confirmed as being capable of favorable recovery of CF₄, C₂F₆, and NF₃.

[0061]

20 Tests were also conducted using F-9 (manufactured by Tosoh Corporation), which is described as having a similar structure to molecular sieve 13X (an equivalent product), as the zeolite 30. This F-9 enabled separation of CF₄ and C₂F₆ in a similar manner to that observed for the molecular sieve 25 13X, although the retention times were marginally longer.